CARBON DIOXIDE CONTENT OF MINE-FIRE ATMOSPHERES AS AN AID WHEN FIGHTING METAL-MINE FIRES

BY S. H. ASH

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by

S. H. Ash[2]

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[2] Chief, Safety Branch, Health and Safety Division, Bureau of Mines, Washington, D. C.

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INTRODUCTION

Mine fires have occurred since underground mining of minerals began, and they are still occurring. The technical literature is replete with papers relating to mine fires.

Means and methods for controlling and extinguishing mine fires and preventing explosions and other accidents require the collection and analyses of samples of the atmospheres surrounding the fire. Such atmospheres are complex mixtures of gases (1, 3, 4, 15, 21, 23).[3]

SUMMARY

Experiences at mine fires (1, 3, 4, 15, 21, 23) have proved conclusively that mine-air analyses furnish the only means of judging what is going on in a mine-fire area. Mine-air analyses give evidence of conditions that require immediate protection, govern the order and control the manner in which a fire is fought, show the necessity of bulkheads and establish the places to construct them, indicate whether or not a fire is being controlled or is being extinguished, and govern procedure in sealing and unsealing mine fires.

It is commonly believed that danger to life and property from mine-fire atmospheres is greatest in coal mines; this is true only to the degree that the explosion hazard is greater in coal mines than in noncoal mines because of the presence of combustible gases. The problem of gas poisoning is greater in noncoal mines because of the more frequent occurrence of poisonous and innocuous gases, oftentimes the lack of controlled ventilation, and usually greater difficulties in sealing mine-fire areas. Sulfide minerals present a serious hazard in many metal-mine fires when sulfur dioxide is formed. The country rock or ore body itself may contain or be limestone, which may be calcined. Emanations of carbon dioxide are found.

A fire in a confined place presents a hazard from explosion wherever the fire occurs, whether in a building, a metal mine, a coal mine, a tunnel, or an industrial plant. The degree of hazard depends upon the gases that are present, and the method of dealing with a particular problem can be modified according to the gaseous constituents present.

It has been observed that the percentage of oxygen in the air in a mine-fire atmosphere or a normal mine atmosphere changes only slightly or

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[3] Figures in parentheses refer to items in the bibliography at the end of this report.

not at all when adsorption of the oxygen by the strata is completed and oxidation from heat ceases. Any change in the oxygen content at this point is accomplished by dilution of the mine atmosphere by emanations of gas such as methane, carbon dioxide, or other gases. For this reason the progress of a mine fire can best be analyzed and sometimes can only be determined by a study of the air-free analyses of the mine-fire atmosphere.

When a mine-fire area is sealed, the experience of the author supports reducing the oxygen content of the fire area as soon as possible to below 16 percent (when flaming of timber ceases) and the advisability of maintaining a nonexplosive atmosphere on the return-air side of a mine fire by allowing, and aiding if possible, the inert gases from the fire to increase until the oxygen content of the atmosphere on that side is less than the critical oxygen value of that atmosphere. This is accomplished by (a) first sealing the openings on the return-air side of a fire area, (b) maintaining a nonexplosive atmosphere on the intake-air side of the fire, and (c) sealing the intake-air openings last.

The carbon dioxide content of a mine-fire atmosphere is significant. For certain types of fires and mines it ultimately reaches a fairly constant high value during an active fire as well as a fairly constant lower value after the fire is extinguished. It provides a valuable criterion on the progress of a fire in steeply dipping mine workings and in metal mines. When the fire is extinguished, the fire gases, on cooling, permit the carbon dioxide to settle rapidly into the lower workings and, by diffusion, to become fairly constant ultimately throughout the area under seal (3, 9).

The carbon dioxide content of the air-free composition of a mine-fire atmosphere shows a definite trend downward when a fire is being extinguished. When the fire is out, a line constructed of points corresponding to the carbon dioxide content on an air-free basis flattens, and, in a tightly sealed area, the carbon dioxide content is almost constant. Because of its magnitude (as compared with the carbon monoxide content), the carbon dioxide content (air-free) can be the means of indicating whether or not a fire is out, after analyses show that carbon monoxide is absent. If methane is being generated, the carbon dioxide content on an air-free, methane-free basis can be used for the foregoing purpose. (See fig. 3).

A high dilution of the fire gases with air decreases the accuracy of deduction from "as received" analyses. However, air-free analyses of the effluent gases from a wood fire show a definite pattern from which deductions can be made. If sulfide minerals, limestone, or strata-gas are present, they must be considered in making deductions from the analyses of the mine-fire gas in a sealed area.

Figure 4 shows the time-carbon dioxide-percent curves of a mine-fire atmosphere in an iron mine after the fire area was sealed.

The fire area was unsealed on January 19, 30 days after it was sealed. The fire was out, and the mining operations were resumed. The oxygen content of the mine-air samples collected in the fire area ranged from a high of 16.24 to a low of 3.20 percent and the carbon monoxide from 0.15 to 0.00

percent. The carbon monoxide gradually increased until the fourteenth day after the area was sealed, after which a definite decrease was observed. No carbon monoxide was detectable 17 days after the fire area was sealed.

Figures 5 and 6 show the time-carbon dioxide-percent curves of a mine-fire atmosphere in a lead-zinc mine where the temperature in the sealed fire area rose above the calcination temperature of limestone (800° to 900° C.). Each curve represents the average of samples collected at several sampling positions on each level.

The curves on figure 5 show that the carbon dioxide continued to rise from 15 percent at the time of sealing to a maximum of more than 22 percent in August 1946. Slimes were pumped through seals on the 17th and 18th levels to fill the stoped area containing the burning materials. The curves in figures 5 and 6 indicate that active combustion and heating ended in August 1946. They show that the percentage of carbon dioxide remained nearly constant or dropped slowly until the opening made in July 1947 to the 17th level permitted more rapid dilution of the effluent gases. In November 1947 the fire area apparently had cooled enough to allow the heavier carbon dioxide to settle to the 20th level, and a few samples collected in August and November 1948 showed a gradual increase in the carbon dioxide content in the area below the fire.

Figure 7 shows the time-carbon dioxide-percent curves of a mine-fire atmosphere in the same lead-zinc mine where mine-air samples collected indicate that the temperature in the fire area did not reach the calcination temperature of the limestone country rock. Each curve on figure 7 represents the average of samples collected at several sampling positions on each level.

It would appear that active combustion ended very soon after the fire was sealed, and that the fire area had cooled to nearly normal temperature in September 1943.

The presence of sulfur dioxide in mine-fire atmospheres often make deductions from analyses difficult or even impossible. High sulfur dioxide can be present in a mine-fire atmosphere, and it will not be possible to determine its percentage. Where this happens, sulfur dioxide can be a predominant gas, and its formation will reduce the percentage of other gases, such as carbon dioxide, to a degree that renders the time-carbon dioxide-percent curve difficult to interpret. This is accomplished indirectly, for the most part, by the sulfur combining with the oxygen in the air to form SO_2, which is not determined analytically and is shown as nitrogen. Nitrogen appears to be the predominant gas in the analysis, whereas its true percentage is not determined analytically.

It is not possible to make an analysis for sulfides or sulfur dioxide when samples are collected in vacuum bottles, by water displacement, or by aspirating devices and sampling bottles. It would be necessary to analyze samples for sulfides and sulfur dioxide at the source, as analysis of transmitted samples is impossible.

As far as the author knows, no studies have been made to correlate the progress of a mine fire in terms of sulfide or sulfur dioxide; hence, the interpretation of the analyses for these gases would be difficult. Ostwald combustion charts and the Pigrais chart are useful in combustion work and may have some application in the determination of SO_2 (7, 19, 24, 25) in some metal-mine-fire atmospheres. It would be interesting for someone to make a study in the field with laboratory methods for sulfides and sulfur dioxide to see if there is any trend in their percentages after sealing a mine-fire area. Such a problem would be in the nature of research rather than routine analysis.

A fire was discovered on February 15, 1938, in the underground workings of the Argonaut mine, Jackson, Calif. This fire has been described briefly. The mine fire occurred on the 4,350-foot level from an unknown cause. It was sealed on February 26, 11 days after it was discovered. Natural rock temperature in the lower mine workings is 92° F.

The importance of deductions from analyses of mine-fire atmospheres and from the pressure exerted by them on seals in a mine-fire area is not always realized. Whether the pressure on a seal is positive or negative depends primarily on the difference between the specific gravities of the atmospheres on opposite sides of the seal. A cooled mine-fire atmosphere sometimes becomes heavy enough to overcome the normal ventilating motive column.

Because of the differences in magnitude of the specific gravity and percentage of the respective simple gases composing a mine-fire atmosphere, the air-free compositions of different portions of an atmosphere confined in a place with which the mine-fire atmosphere is mixing by convection and diffusion differ from each other and from the air-free mine-fire atmosphere. For this reason it is often desirable to know the specific gravity of portions of the sealed atmosphere (3).

Purpose of Report

The purpose of this report is to show briefly how to utilize the trend of the carbon dioxide content of mine-fire atmospheres to fight metal-mine fires.

Ash and Felegy have discussed much detail and give an extensive bibliography pertaining to the application of analyses of complex mixtures of gases to control and extinguish fires and to prevent explosions in mines, tunnels, and hazardous industrial processes (2, 3).

Mine fires may be extinguished by fighting directly and utilizing water or chemicals; by flooding with water, inert gas, or mixtures of water and solids (4, 12, 22, 26); by excavating the heated material; by sealing the fire area (3); or by combinations of the foregoing methods.

This paper discusses matters concerned with the control and extinguishment of some metal-mine fires that were sealed and suffocated thereby. Because emanations of combustible gases from the strata are not common in metal mines, although they are by no means unknown (17), they are mentioned briefly.

VALUE OF GAS ANALYSIS

Experiences at mine fires (1, 3, 4, 15, 21, 23) have proved conclusively that mine-air analyses furnish the only means of judging what is going on in a mine-fire area. Mine-air analyses give notice of conditions that require immediate protection, govern the order and control the manner by which a fire is fought, show the necessity of bulkheads and establish the places to construct them, indicate whether or not a fire is being controlled or is being extinguished, and govern procedure in sealing and unsealing mine fires.

Sampling and Analyzing Atmospheres

Close relationship exists between the composition of the atmosphere and problems of health and safety in mines, tunnels, and other confined places where explosive or poisonous gases may be present. This interdependency makes sampling and analysis of the atmosphere the most important part of the safety work in these places.

The collection of a representative sample and the preservation of that sample until it can be analyzed are the most important and most difficult parts of the procedure in determining the composition of a dangerous atmosphere. Inaccurate sampling gives erroneous results. Erroneous results, which lead to incorrect interpretations and conclusions, may cause a false sense of security and may be used as a basis for unsafe or unnecessary recommendations.

A complete description of the methods of sampling and analysis of mine, tunnel, or other atmospheres is given in publications of the Bureau of Mines (6, 8, 27).

MINE-FIRE ATMOSPHERES

The presence of complex mixtures of gases where the control and extinguishment of fires is being attempted not only adds to the confusion and difficulties of fire-fighting operations but may create greater hazards than are recognized by those persons responsible for the direction of fire-fighting activities, unless the full import of the nature of the gases encountered is known.

It is commonly believed that danger to life and property from mine-fire atmospheres is greatest in coal mines. This is true only to the degree that the explosion hazard is greater in coal mines than in noncoal mines because of the presence of combustible gases. The problem of gas poisoning is greater in noncoal mines because of the more frequent occurrence of poisonous and innocuous gases, oftentimes the lack of controlled ventilation, and usually greater difficulties in sealing mine-fire areas. Sulfide minerals present a serious hazard in many metal-mine fires when sulfur dioxide is formed. The country rock or ore body itself may contain or be limestone, which may be calcined. Emanations of carbon dioxide are encountered.

Although methane is likely to occur in any coal mine, the metal mines of the world contain by far a greater variety of gases than do the coal mines. Often, the gases in metal mines are as dangerous as the gases likely to be found in coal mines, and sometimes they are even more deadly (17).

Emanations of gases from the strata are found in many metal mines and tunnels (17). Methane is frequently found in gold, gold-silver, lead-zinc, and potash mines (5, 17). Nitrogen, carbon dioxide, and hydrogen sulfide are found in many mines and tunnels (11, 14, 16, 17).

The subject relating to the determination of the explosive limits of gases and vapors has been fully covered by Coward and Jones, who also present the results of a critical review of all figures published (as of February 1938) on the limits of explosibility of a great number of combustible gases and vapors when admixed with air, oxygen, or other atmosphere (10, 18).

Data relating to the explosibility factors and applied to complex mixtures of gases consisting of carbon monoxide, methane, hydrogen, ethylene, propylene, carbon dioxide, nitrogen, and air have been proved by experiment to apply to the gases stated. Formulas and charts relating to mixtures of these gases have been developed and discussed by Ash and Felegy. The formulas and charts may be extended to include other gases but, in the absence of corroborative test data, cannot be assumed to apply indiscriminately to all combustible gases.

A fire in a confined place presents a hazard from explosion wherever the fire occurs, whether in a building, metal mine, coal mine, tunnel, or an industrial plant. The degree of hazard depends on the gases that are present, and the method of dealing with a particular problem can be modified according to the gaseous constituents present.

If considerable carbon dioxide is present, and emanations of other gas, such as methane, are absent, carbon dioxide eventually becomes the dominant constituent of the mine-fire atmosphere; in combination with nitrogen, it eventually creates an extinctive atmosphere by reducing the oxygen content and assists very materially in extinguishing the fire by depriving it of oxygen. Nitrogen is usually the dominant constituent of metal-mine fire atmospheres that are sealed.

To understand more clearly the significance of complex gas mixtures or the effects of admixing a diluent, or additional inert gas, with an atmosphere that may or may not have explosive limits with air, an atmosphere may be considered to consist possibly of three parts: (a) the gas portion (gas), or a mixture of simple combustible gases and simple inert gases such as nitrogen and carbon dioxide; (b) a portion (air) consisting of normal air; and (c) a portion considered as diluent that, unless stated otherwise, consists of additional inert gas, which may be nitrogen or carbon dioxide. (See figs. 1 and 2).

An original atmosphere can be considered as one in which the additional-inert-gas portion is absent, i.e., an original atmosphere is considered

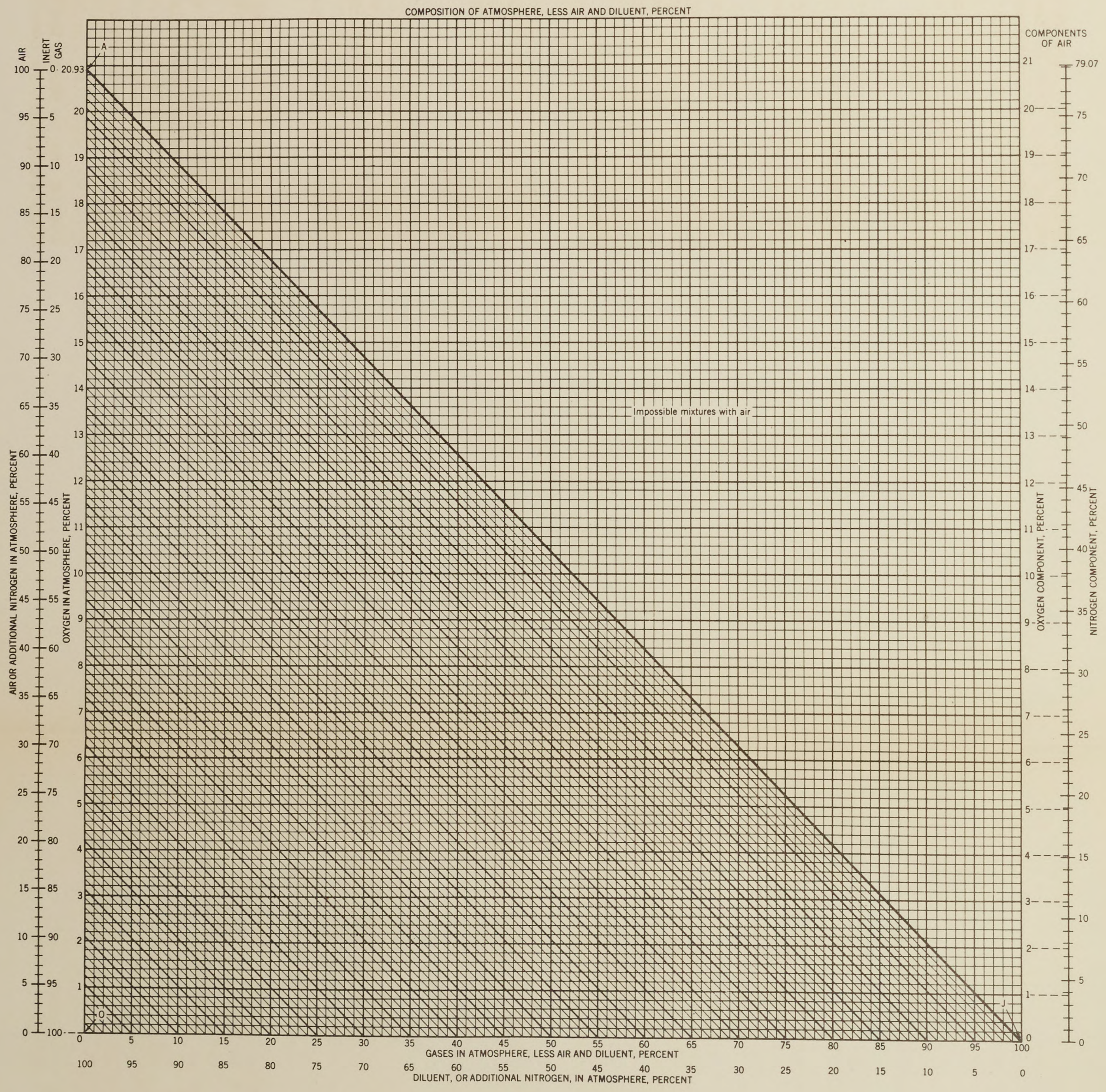

Figure 1. - Relation between various constituents of any possible gaseous mixture composed of a combustible gas or combustible gases, different volumes of carbon dioxide and nitrogen, and air.

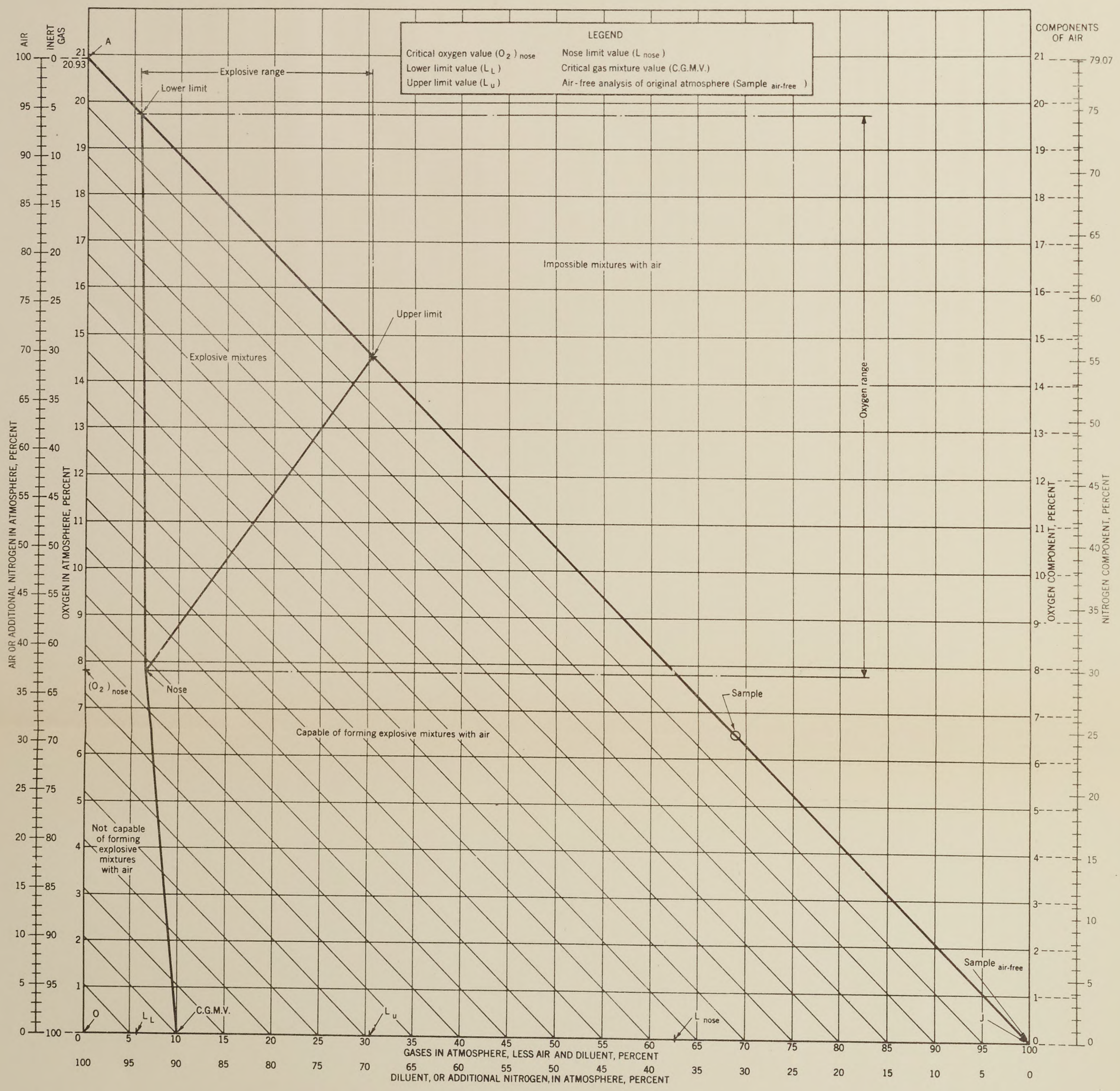

Figure 2. - Relation between factors expressing composition and explosibility of a mixture composed of equal proportions of carbon monoxide, methane, and hydrogen, and nitrogen and air.

as diluent-free. An air-free original atmosphere, therefore, consists only of the gas portion.

Changes occur in normal atmospheric air from various causes as it courses through underground passageways (3, 23). Normal mine air is air that is ordinarily classed as good air for underground atmospheres, or it is the air in a mine operating under normal conditions. The composition of normal mine air is not the same in all types of underground mines.

The following analyses are an average of the percentages of the simple gases composing mine atmospheres that were sampled and analyzed by the Bureau of Mines. They are representative of atmospheres that are considered to be normal mine air.

Normal mine atmospheres (average analyses), percent

Constituent (simple gas)	Normal atmospheric air	Sub-bituminous-coal mines	Bituminous-coal mines	Anthracite mines	Metal and noncoal mines
Oxygen..............	20.93	20.41	20.53	20.58	20.62
Nitrogen............	78.10	79.21	79.12	79.03	79.19
Carbon dioxide......	.03	.23	.17	.22	.19
Methane.............	.00	.15	.18	.17	.00
Other gases.........	1/.94	2/	2/	2/	2/

1/ Argon.
2/ Considered as nitrogen.

The average analysis, which consists of the average percentage of each simple gas, does not necessarily define the normal mine air throughout the average mine nor the composition of the most probable normal mine atmosphere in the ordinary coal mine, metal mine, or tunnel.

The most probable content (in percent) of the simple gases composing normal mine atmospheres is the percentage of each simple gas that occurs in the greatest number of samples from representative mines. The most probable normal mine atmospheres of underground mines are shown in the following table:

Most probable normal mine atmospheres in ordinary mines, percent

Constituent (simple gas)	Normal atmospheric air	Sub-bituminous-coal mines	Bituminous-coal mines	Anthracite mines	Metal and noncoal mines
Oxygen..............	20.93	20.59	20.71	20.72	20.76
Nitrogen............	78.10	79.22	79.14	79.14	79.16
Carbon dioxide......	.03	.18	.13	.12	.08
Methane.............	.00	.01	.02	.03	.00
Other gases.........	1/.94	2/	2/	2/	2/

1/ Argon.
2/ Considered as nitrogen.

It can be seen from the data in the foregoing table that the composition of the air in the ordinary operating mine does not differ greatly from that of normal atmospheric air. When dealing with a mine fire, the composition of the normal mine air can be determined only by analyses of representative samples of the atmosphere in the mine concerned.

AIR-FREE COMPOSITION OF MINE ATMOSPHERE

The oxygen content of a mine atmosphere must come from the atmospheric air that enters the mine. For this reason, moisture-free mine air can be considered as consisting of pure atmospheric air and other simple gases. Furthermore, it can be concluded that the simple gases generated or liberated in a mine, from whatever source, are diluted by air, and that they existed originally in their pure state at some point in the mine.

In a tightly sealed mine-fire area, the mine-fire atmosphere is depleted of oxygen by adsorption of oxygen by the mineral in contact with the air and by oxidation processes, a knowledge of the nature of which is not necessary in this discussion. The air remaining is diluted by emanations of gas, if the strata contain gas under pressure.

In a newly sealed mine-fire area, the atmosphere contains the least oxygen at the place where the fire is burning. The rate at which the fire gases are diluted decreases with the distance from the fire because of dilution and diffusion of the fire gases by the surrounding mine air. If a sample of the mine-fire atmosphere is taken at any point within the sealed area, the maximum percentage of each simple gas as it existed before dilution with air is the percentage of the simple gas in the atmosphere when all the air is removed. This is the air-free analysis of the sample.

It has been observed that the percentage of oxygen in the air in a mine-fire atmosphere or a normal mine atmosphere changes only slightly, or not at all, when adsorption of the oxygen by the strata is completed and oxidation from heat ceases. Any change in the oxygen content at this point is accomplished by dilution of the mine atmosphere by emanations of gas such as methane, carbon dioxide, or other gases. For this reason, the progress of a mine fire can best be analyzed and sometimes can only be determined by a study of the air-free analyses of the mine-fire atmosphere.

In sealed mine-fire areas that generate considerable methane, dilution of the mine-fire atmosphere by methane becomes important. If this is accomplished without an explosion, methane becomes the dominant constituent of the mine-fire atmosphere; and, by reducing the oxygen content, it eventually creates a nonexplosive atmosphere and assists very materially in extinguishing the fire by depriving it of oxygen.

If considerable methane is present, the air-free, methane-free analyses will give information from which the most reliable trend of the fire can be determined.

Analyses of mine-fire atmospheres are made, and often little or no value is attached to them because of variations in the percentages of the simple gases. In the vast majority of instances, it is found that the differences in these percentages are caused by nothing more than corresponding differences in the air content of the samples. This may result from admission of air during sampling or during analysis; or it may be the effect of barometric pressure on emanations of gas such as methane, carbon dioxide, or nitrogen, and on breathing at seals. If the analyses of a series of samples taken at approximately the same time are calculated to an air-free basis, the percentages of the simple gases are usually found to be approximately the same.

CALCULATION OF AIR-FREE ANALYSIS

A step of prime importance in determining what is going on in a mine-fire area from the analyses of mine-fire atmosphere is calculation, to an air-free basis, of the analysis of the atmosphere sampled. This is done by first considering all the oxygen in the sample as a component of normal atmospheric air.

Normal atmospheric air contains 20.93 percent of oxygen, by volume. For all practical purposes, the other gases (carbon dioxide and argon) can be considered as nitrogen. The volume of air in the atmosphere sampled is expressed by the following formula:

$$\text{Air}_s = \frac{(O_2)_s\ (100)}{20.93} \text{ percent,} \qquad \text{(A)}$$

where (Air_s) and $(O_2)_s$ are the volumes (in percent) of air and oxygen, respectively, in the atmosphere sampled.

As the atmosphere sampled consists of air and other gases, the volume of gases (K_s) other than air can be expressed, in percent, as follows:

$$K_s = (100 - \text{Air}_s) \text{ percent.}$$

By substituting equation (A) in the expression above, the volume of the air-free mixture (gases other than air) can be determined by the following formula:

$$K_s = 100 - \frac{(O_2)_s\ (100)}{20.93} \text{ percent.} \qquad \text{(B)}$$

When the respective volumes (in percent) of the simple gases, except nitrogen and oxygen, composing the atmosphere sampled are divided by the total volume (K_s) of the simple gases other than air, as obtained by equation (B), and each of these volumes is then multiplied by 100, the air-free volumes (in percent) of the simple gases, except the nitrogen, are obtained.

The volume of nitrogen $(N_2)_1$ on an air-free basis is the difference between 100 and the sum (Σ) of the volumes of the other simple gases (air-free basis). The volume of nitrogen $(N_2)_1$ on an air-free basis can also be found by formula (E), which has been derived by considering the total nitrogen $(N_2)_s$ as consisting of two parts - one $(N_2)_{air-s}$ derived from the air and the other $(N_2)_{gp-s}$ as a constituent of the gas portion (Gas_s) of the atmosphere sampled. Equations expressing the volume of each simple gas, calculated to an air-free basis, are:

$$\text{Constituent}_{\text{air-free}} = \frac{\text{Constituent}_s}{K_s}(100), \qquad (C)$$

and

$$(N_2)_1 = 100 - \varepsilon, \qquad (D)$$

or

$$(N_2)_1 = \frac{((N_2)_s - \text{Air}_s + (O_2)_s)(100)}{K_s} \qquad (E)$$

where $\text{Constituent}_{\text{air-free}}$ is the volume of each simple gas, except nitrogen, on an air-free basis; $(N_2)_s$ is the total amount of nitrogen in the sample; ε is the total volume of the individual constituents, except the nitrogen, in the air-free analysis of the atmosphere sampled; and the other symbols have the same meanings as before.

The method by which the air-free composition of a complex gas mixture is determined is shown below. An atmosphere beneath a building in which an explosion had occurred is used as an example. The sample represents the composition of the atmosphere (carbureted water gas and air) in a sealed area beneath the building.

The compositions of the atmosphere as sampled, and when calculated to an air-free basis, are as follows:

Constituent	Analysis of sample as collected		Air-free analysis	
	Percent	Symbol	Percent	Symbol
Carbon dioxide.................	3.90	D_s	4.00	D_1
Ethylene.......................	5.76	$(C_2H_4)_s$	5.92	$(C_2H_4)_1$
Propylene......................	1.44	$(C_3H_6)_s$	1.48	$(C_3H_6)_1$
Methane........................	11.25	B_s	11.55	B_1
Hydrogen.......................	42.95	$(H_2)_s$	44.11	$(H_2)_1$
Carbon monoxide................	31.30	A_s	32.14	A_1
Oxygen.........................	.55	$(O_2)_s$	.00	-
Nitrogen, total................	2.85	$(N_2)_s$	.80	$(N_2)_1$
Air............................	2.63	$(\text{Air})_s$	.00	-
Nitrogen in air................	2.08	$(N_2)_{\text{air-s}}$	.00	-
Gases other than air..........	97.37	K_s	100.00	-

The volume of air (Air_s) in the atmosphere sampled is found by substituting the volume of oxygen (0.55 percent) in the sample for the corresponding symbol in formula (A) as follows:

$$\text{Air}_s = \frac{(O_2)_s\ (100)}{20.93} = \frac{0.55 \times 100}{20.93} = 2.63 \text{ percent.}$$

From formula (B) we obtain the percentage (K_s) of the gases other than air in the atmosphere sampled; this is a constant used to determine the percentages of simple gases, or constituents, composing the atmosphere under consideration:

$$K_s = 100 - Air_s = 100 - 2.63 \text{ percent} = 97.37 \text{ percent.}$$

To determine the volume of each simple gas of the air-free analysis, determination of the hydrogen $(H_2)_1$ (air-free) can be used as an example. By substituting the volume of hydrogen $(H_2)_s$, as determined by analysis, for the corresponding symbol in formula (C), we find

$$(H_2)_1 = \frac{(H_2)_s\ (100)}{K} \quad \frac{42.95 \times 100}{97.37} = 44.11 \text{ percent.}$$

The percentages of the other simple gases, on an air-free basis, are found in a similar manner, with the exception of the percentage of nitrogen $(N_2)_1$, which is found by substituting the real values of the other simple gases for the symbols in formula (D), as follows:

$$\begin{aligned} (N_2)_1 &= 100 - \Sigma\ , & \text{(D)} \\ &= 100 - D_1 + (C_2H_4) + (C_3H_6)_1 + B_1 + (H_2)_1 + A_1, \\ &= 100 - (4.00 + 5.92 + 1.48 + 11.55 + 44.11 + 32.14), \\ &= 100 - 99.20 = 0.80 \text{ percent;} \end{aligned}$$

or from formula (E)

$$(N_2)_1 = \frac{((N_2)_s - Air_s + (O_2)_s)(100)}{K_s} \qquad \text{(E)}$$

$$= \frac{(2.85 - 2.63 + 0.55) \times 100}{97.37} = 0.80 \text{ percent.}$$

EXTINGUISHING MINE FIRE BY SEALING

When it is decided to seal a fire area, the success of the work will depend solely on the effectiveness of the methods and facilities utilized to seal and extinguish the fire; and the measure of ultimate success will be attained only when the carbon monoxide content of the atmosphere within the fire zone is reduced to zero. However, physical conditions and other features attending each fire must be considered in deciding positively, on the basis of the disappearance of carbon monoxide, that a fire has been extinguished. There is one conclusion that can be generally accepted - that, with continued exclusion of oxygen and cooling of strata and other combustible materials for some time after the carbon monoxide is gone, the fire will be extinguished ultimately. Time is important.

In general, each fire should be investigated separately. Ash, Felegy, Forbes, Grove, Maize, Walsh, and Scott have discussed suggested procedure in unsealing mine fires in recovery operations (3, 13, 20, 23).

When a mine-fire area is sealed, the experience of the author supports reducing the oxygen content of the fire area as soon as possible to below 16 percent (when flaming of timber ceases) and the advisability of maintaining a nonexplosive atmosphere on the return-air side of a mine fire by allowing, and aiding, if possible, the inert gases from the fire to increase until the oxygen content of the atmosphere on that side is less than the critical oxygen value of that atmosphere. This is accomplished by (a) sealing first the openings on the return-air side of a fire area, (b) maintaining a nonexplosive atmosphere on the intake-air side of the fire, and (c) sealing the intake-air openings last.

When fighting a mine fire, the first consideration is to prevent an explosion. Explosions may occur while a fire is being fought directly, when a fire area is being sealed, after an area has been sealed, or when a mine-fire area is unsealed. Finally it is important to know when a mine fire has been extinguished and whether the mine-fire area can be unsealed safely.

In any mine fire, knowledge of the volumes of carbon dioxide, carbon monoxide, and hydrogen (in coal mines) present in the atmosphere are of far more value for indicating the progress of the fire than knowledge of the amount of oxygen present. The carbon dioxide, carbon monoxide, and hydrogen contents of the mine-fire atmosphere follow fairly definite trends, whereas the oxygen content is variable.

The oxygen percentages of mine-fire gas samples taken at the same place vary markedly from day to day, although it is known that the heated area from which the gases come could not be affected appreciably in the time involved. In large sealed areas, in broken and fissured ground, in extensive workings, or in areas where many seals are present, infiltration of air oftentimes cannot be prevented. Under such conditions a fire area will breathe, and it is necessary to correct this condition if a fire is to be suffocated. The outstanding values of the oxygen content are (a) the knowledge that it is above or below the percentage (the critical oxygen value) at which an explosion can occur, (b) the indication given by decreasing oxygen content that an area is being sealed effectively, and (c) that flames are not present to spread the fire. With suitable reservations, the oxygen content can serve as a criterion of the proportion of excess air that is present.

Carbon monoxide is a product of combustion, and it exists in a fire area only when an active fire is in progress or has been present, with or without flame. It is difficult to ascertain the exact conditions of a fire from the percentage of carbon monoxide present. The percentage of carbon monoxide is highest at high temperatures when the volatile constituents become active in combustion, and lowest either when there is no fire or when there is perfect combustion. (See fig. 3.)

The carbon dioxide content of a mine-fire atmosphere is significant. For certain types of fires and mines it ultimately reaches a fairly constant high value during an active fire as well as a fairly constant lower value after the fire has been extinguished. It provides a valuable criterion on the progress of a fire in steeply dipping mine workings and in metal mines. When the fire is extinguished, the fire gases, on cooling, permit the carbon

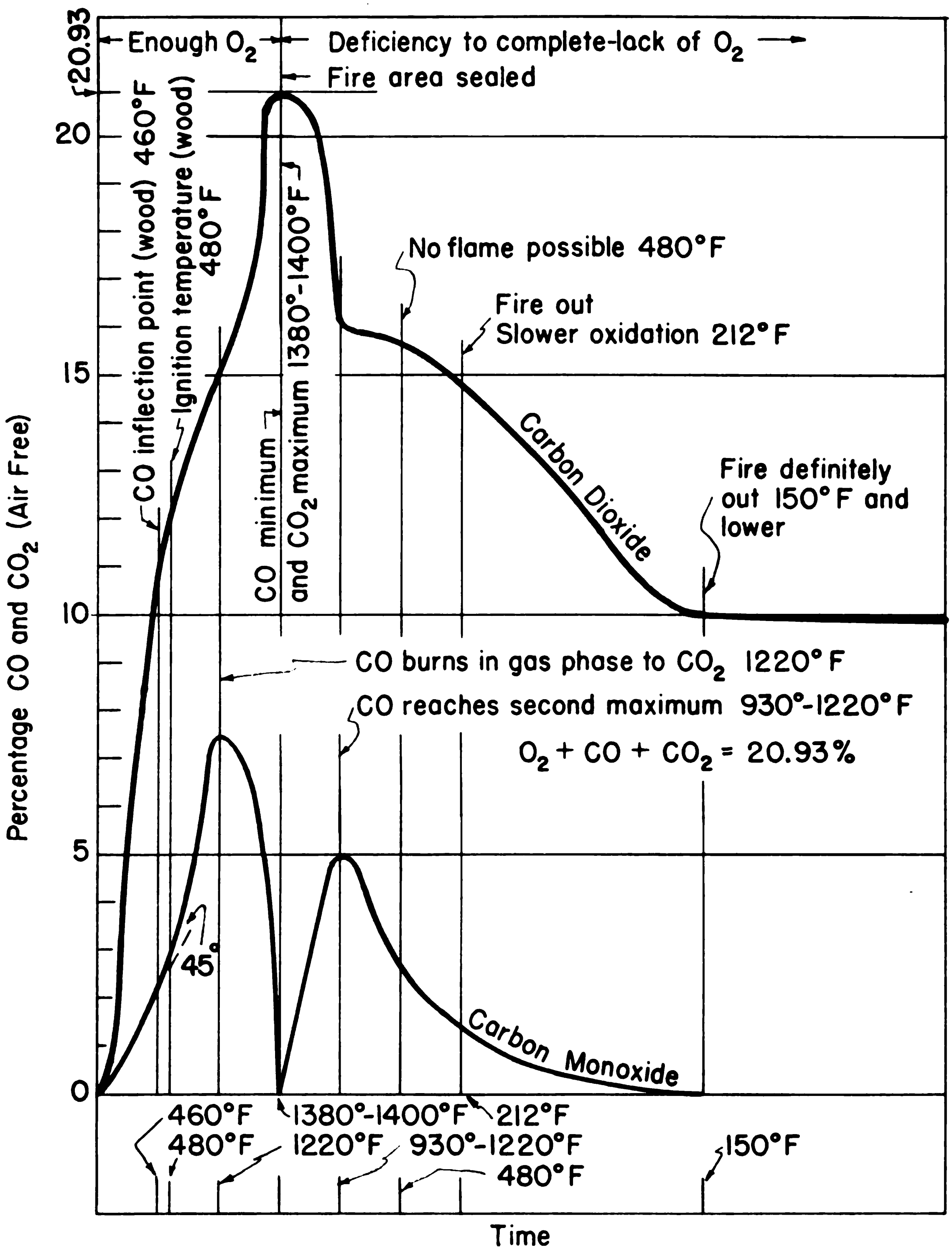

Figure 3.— Time-percent curves (carbon dioxide and carbon monoxide) under ideal conditions of wood fire, before sealing mine fire area and after sealing it. (not to scale)

dioxide to settle rapidly into the lower workings and, by diffusion, to become fairly constant ultimately throughout the area under seal (3, 9).

The carbon dioxide content of the air-free composition of a mine-fire atmosphere shows a definite trend downward when a fire is being extinguished. When the fire is out, a line constructed of points corresponding to the carbon dioxide content on an air-free basis flattens; and, in a tightly sealed area, the carbon dioxide content is almost constant. Because of its magnitude (as compared with the carbon monoxide content), the carbon dioxide content (air-free) can be the means of indicating whether or not a fire is out after analyses show that carbon monoxide is absent. If methane is being generated, the carbon dioxide content on an air-free, methane-free basis can be used for the foregoing purpose. (See fig. 3.)

It appears that too much stress is placed on analyses of samples "as received" to indicate either the progress of a fire or the atmospheric condition existing in a sealed area. A more accurate picture is presented by the compositions of the samples on an air-free basis. Samples highly contaminated with air give a reliable trend of the fire only by comparing the composition of the samples on an air-free basis.

The following discussion briefly covers some observations regarding analyses of selected mine-fire atmospheres that are of interest.

Because carbon monoxide is usually considered a definite criterion when studying mine fires, it must be realized that the presence of carbonaceous materials is necessary to have it formed. The presence of other gases due to strata-gases or heat can and does interfere materially with the utility of carbon monoxide as a criterion for determining the progress of a fire by either its presence or its absence.

Figure 3 shows ideal conditions (concerning carbon dioxide and carbon monoxide) surrounding a wood fire to the point where the fire area is sealed. What takes place after a fire is sealed is conjectural, as is shown by the analyses of some typical metal mine-fire atmospheres and by figures 4 to 7, inclusive. Other oxidation products need not be considered in determining the progress of a wood fire.

Although wood usually is the constituent burned in metal-mine fires, some of the most serious fires in metal mines have been those in which electrical equipment (insulation, principally) and petroleum products were burned. Sulfur dioxide is present when sulfide minerals are heated and burned.

Where wood is burning with free access of air, that is, where the fire area is unsealed, the principal effluent gases formed by the fire are carbon dioxide and carbon monoxide. As the problem is concerned principally with extinguishing the fire, only those gases need be considered in this discussion, although hydrogen is an important factor in the determination of temperatures in a coal-mine-fire area (3, 23).

Until the "carbon monoxide inflection point" is reached, the oxidation proceeds in direct proportion to the temperature, and the time-carbon dioxide-percent curve and time-carbon monoxide-percent curve can be considered as lines increasing in slope. According to Scott (23), the carbon monoxide inflection point is that point at which the carbon monoxide content of the effluent gases from the fuel bed changes from a slowly increasing to a rapidly increasing percentage, or the point at which the tangent to the time-carbon monoxide-percent curve is 45°. The carbon monoxide inflection point for wood can be considered as 460° F., or 240° C. Oxidation proceeds rapidly after the carbon monoxide inflection point is reached, with a resultant increase in the carbon monoxide percentage and corresponding decrease in the carbon dioxide percentage until the ignition temperature, approximately 480° F. (250° C.), is reached, when the carbon monoxide percentage rapidly increases.

At 1,220° F. (660° C.), the carbon monoxide percentage reaches its maximum and is burned in the gas phase at this temperature and higher temperatures. As a consequence, the carbon dioxide percentage increases as the temperature increases, with a corresponding decrease in the carbon monoxide percentage, ignoring any producer-gas reaction. This condition can continue until the carbon dioxide percentage of the effluent gases reaches its theoretical maximum of 20.93 percent and the carbon monoxide becomes zero at a temperature of 1,380° to 1,400° F.

If the fire area then is effectively sealed, the gases within the sealed area would normally circulate (by convection) within the sealed area. Owing to oxygen depletion and heat dissipation, the effective temperature would decrease. The carbon dioxide percentage decreases and the carbon monoxide percentage increases as diffusion and circulation within the area continue. The carbon monoxide percentage reaches a second maximum as the temperature ranges from 1,220° to 930° F. The time-carbon dioxide-percent curve flattens, and the carbon monoxide percentage drops rapidly until a temperature of 480° F. is reached. At and below this temperature no flaming occurs. As the area cools the carbon dioxide and carbon monoxide percentages decrease by circulation, leakage, diffusion, and oxidation of CO by bacteria (23). When a temperature of 212° F. is reached, the fire is out. Practical considerations such as diffusion and leakage cause rapid disappearance of carbon monoxide, and the time-carbon dioxide-percent curve is affected correspondingly. (See fig. 3.) As the area cools, diffusion and settling of the heavier carbon dioxide gas result in a flat or steeply rising time-carbon dioxide-percent curve, which depends on the position of the place sampled with respect to the fire. At 150° F. the fire is definitely out, and in a matter of time the carbon monoxide will disappear, and the time-carbon dioxide-percent curve will assume a definitely flat trend for the most part in the fire area.

A high dilution of the fire gases with air decreases the accuracy of deduction from "as received" analyses; however, air-free analyses of the effluent gases from a wood fire show a definite pattern from which deductions can be made. If sulfide minerals, limestone, or strata-gas are present, they must be considered in making deductions from the analyses of the mine-fire gas in a sealed area.

FIRE IN IRON MINE

Figure 4 shows the time-carbon dioxide-percent curves of a mine-fire atmosphere in an iron mine after the fire area was sealed.

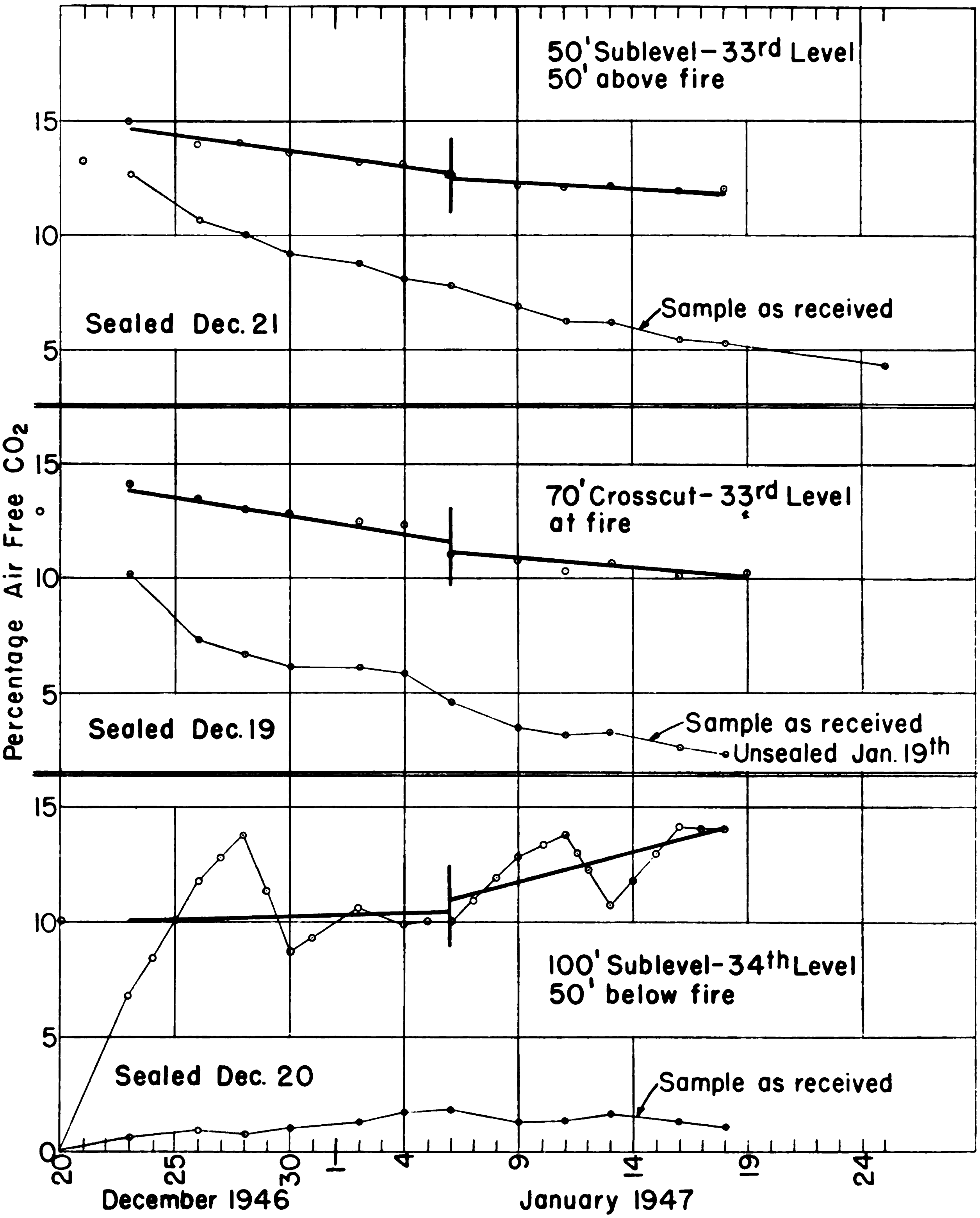

Figure 4.— Showing CO_2 content of mine fire atmosphere in an iron mine.

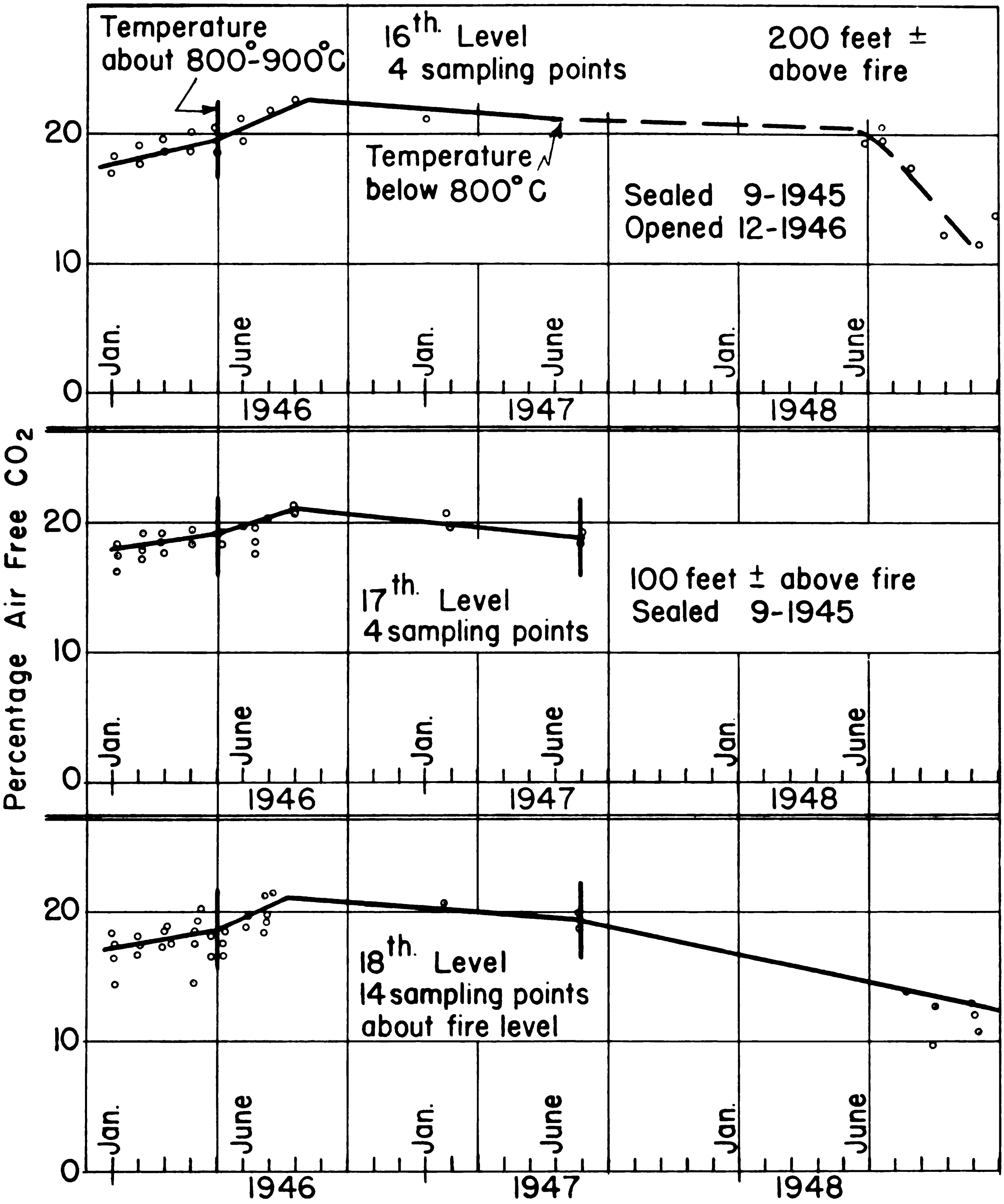

Figure 5.— Showing CO_2 content of mine fire atmosphere in a lead-zinc ore mine in which temperature of fire is above calcination temperature of limestone country rock.

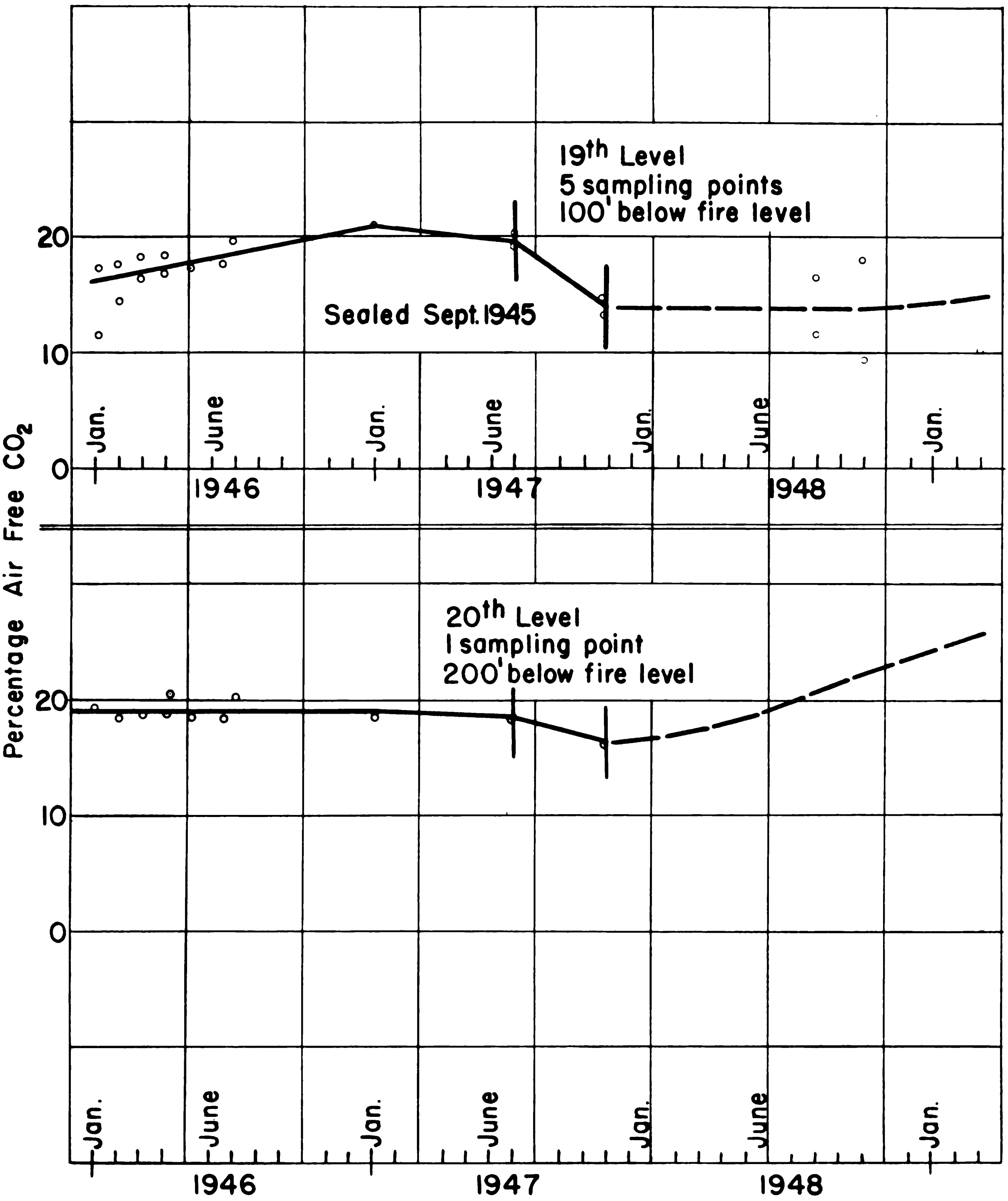

Figure 6.—Showing CO_2 content of mine fire atmosphere in a lead-zinc ore mine in which temperature of fire is above calcination temperature of limestone country rock.—continued from Figure 5.

The main ore bodies in this mine lie in troughs formed by the intersections of intrusive dikes with impervious members of an iron formation, which has a width of 425 feet and dips approximately 62°. The dikes are not continuous across the formation but are interrupted by a longitudinal bedding fault. The ore is classified as soft, and most of it has a claylike consistency with hard ribs throughout. It stands unsupported but breaks fine when blasted. The materials mined and adjoining strata are not subject to spontaneous combustion. Considerable timber is used. The fire is believed to have been caused by a defective light wire or power wire.

The fire could not be extinguished by direct methods, and the area was sealed. This fire is selected as an example of one in which emanations of strata-gas or gases evolved from calcination of limestone or combustion of sulfide minerals were not present.

The fire area was sealed first (December 19) near the fire area, the next day above the fire, and on the second day below the fire. Sampling was started promptly. The time-carbon dioxide-percent curve, both at the fire and above it, trends downward. The curve below the fire trends upward. This shows how the heavier carbon dioxide gas tends to settle in the lower mine workings. The curves show the fire was out on January 6 (17 days later), and the fire area could have been unsealed at that time.

The fire area was unsealed on January 19, 30 days after it was sealed. The fire was out, and mining operations were resumed. The oxygen content of the mine-air samples collected in the fire area ranged from a high of 16.24 to a low of 3.20 percent and the carbon monoxide from 0.15 to 0.00 percent. The carbon monoxide gradually increased until the fourteenth day after the area was sealed, after which a definite decrease was observed. No carbon monoxide was detectable 17 days after the fire area was sealed.

HIGH-TEMPERATURE FIRE IN LEAD-ZINC MINE

Figures 5 and 6 show the time-carbon dioxide-percent curves of a mine-fire atmosphere in a lead-zinc mine where the temperature in the sealed fire area rose above the calcination temperature of limestone (800° to 900° C.). Each curve represents the average of samples collected at several sampling positions on each level.

The main ore bodies in this mine are replacement deposits in limestone; marmatite, galena, pyrite, and siderite are the principal ore minerals. Mining is conducted in underhand square-set stopes. The ore minerals are very friable, and it has been found necessary to mine narrow transverse stopes, usually 5 feet wide, which must be filled before succeeding rows of sets are opened. Some parts of the ore bodies oxidize very rapidly and raise the temperature of the ore, so the practice has been to mine out hot portions of the ore body as rapidly as possible. Ore having a temperature as high as 173° F. has been mined. Although the waste does not fire spontaneously, the timbers remaining in the filled areas present a fire hazard.

On September 24, 1945, smoke was noticed on the 17th level coming from an old filled stope. Seals were constructed progressively in cross cuts leading to this ore body from the 20th level to the 16th level. Sampling of the atmosphere behind the seals was conducted at intervals for several years. The percentage of oxygen in samples collected behind one seal on the 18th level remained comparatively high (15 to 19 percent) through November 1945. After guniting this seal, the percentage of oxygen dropped, indicating that the seal had leaked air for several months before it was gunited. It is possible that the leaks at this point allowed the fire to continue burning and thus permitted the temperature of the material in the filled stope to rise to the calcination temperature of limestone (1,472° F.).

The curves of figure 5 show that the carbon dioxide continued to rise from 15 percent at the time of sealing to a maximum of more than 22 percent in August 1946. Slimes were pumped through seals on the 17th and 18th levels to fill the stoped area containing the burning materials. The curves in figures 5 and 6 indicate that active combustion and heating ended in August 1946. They show that the percentage of carbon dioxide remained nearly constant or dropped slowly until the opening made in July 1947 to the 17th level permitted more rapid dilution of the effluent gases. In November 1947, the fire area apparently had cooled sufficiently to allow the heavier carbon dioxide to settle to the 20th level, and a few samples collected in August and November 1948 showed a gradual increase in the carbon dioxide content in the area below the fire.

FIRE IN LEAD-ZINC MINE

Figure 7 shows the time-carbon dioxide-percent curves of a mine-fire atmosphere in the same lead-zinc mine where mine-air samples collected indicate that the temperature in the fire area did not reach the calcination temperature of the limestone country rock. Each curve on figure 7 represents the average of samples collected at several sampling positions on each level.

This fire was sealed in December 1941, and samples of the atmosphere behind the seals were collected at intervals for a period of 4 years. The percentage of carbon dioxide dropped consistently from January 1942 to September 1943 in the upper levels of the sealed fire area but remained constant in the bottom level in the fire area below the active fire. This indicated gradual cooling of the effluent gases, which permitted the heavier carbon dioxide gas to settle to the lowest level at a rate about equal to the diffusion of the gases throughout the sealed fire area. From September 1943 until the end of 1945, the rate of diffusion of the effluent gases appeared to be about the same throughout the sealed fire area.

It would appear that active combustion ended very soon after the fire was sealed, and that the fire area had cooled to nearly normal temperatures in September 1943.

FIRE IN IRON MINE - PYRITE COUNTRY ROCK

The presence of sulfur dioxide in mine-fire atmospheres often makes deductions from analyses difficult or even impossible. High sulfur dioxide can be present in a mine-fire atmosphere, and it will not be possible to determine its percentage. Where this happens, sulfur dioxide can be a

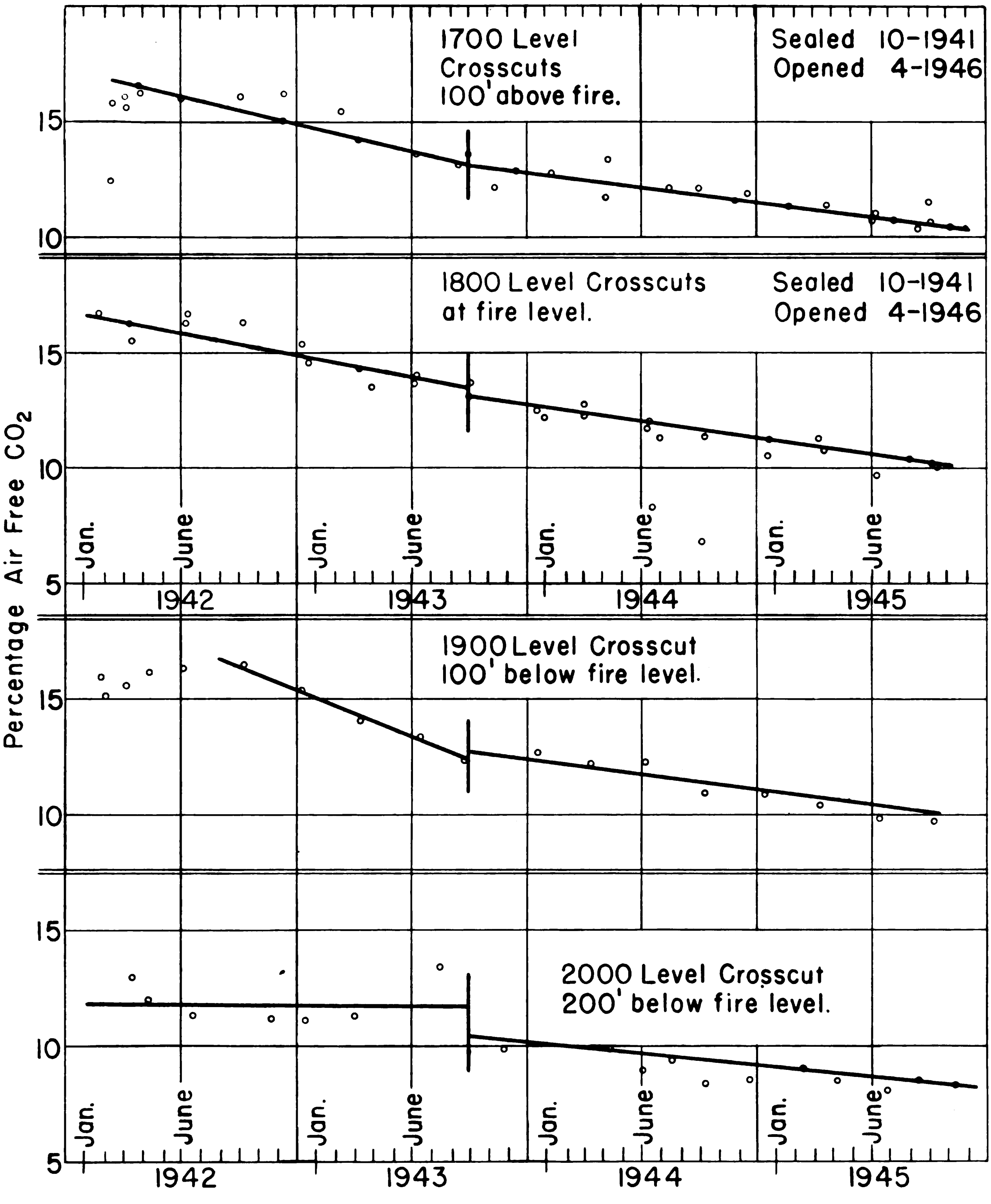

Figure 7 — Showing CO_2 content of mine fire atmosphere in a lead-zinc ore mine in which temperature of fire is below calcination temperature of limestone country rock.

predominant gas, and its presence will reduce the percentage of other gases, such as carbon dioxide, to a degree that renders the time-carbon dioxide-percent curve difficult to interpret. This is accomplished indirectly, for the most part, by the sulfur combining with the oxygen in the air to form SO_2, which is not determined analytically and is shown as nitrogen. Nitrogen appears to be the predominant gas in the analysis, whereas its true percentage is not known.

The following analyses are of an iron-mine-fire atmosphere where the country rock contained considerable pyrite and was in contact with the fire:

Mine-fire analyses (iron mine)

Constituent	Sample 1		Sample 2	
	As received	Air-free	As received	Air-free
Carbon dioxide.........	4.02	4.72	3.91	4.465
Oxygen.................	2.16	.00	2.61	.000
Hydrogen...............	-	-	-	-
Carbon monoxide........	.00	.00	.0025	.003
Methane................	.00	.00	.00	.000
Nitrogen[1].............	93.82	95.28	93.48	95.532

[1] Contains SO_2 not determined by analysis.

It is evident from the foregoing analyses that the atmosphere was depleted of oxygen by the burning of combustible materials other than the carbonaceous materials. It is known that considerable SO_2 was evolved; furthermore, the volume of air remaining in the sealed area was relatively small (10.32 percent in sample 1 and 14.47 percent in sample 2) in relation to the carbon dioxide generated. This fire was extinguished, and the sealed area was reopened.

It is not possible to make an analysis for sulfides or sulfur dioxide when samples are collected in vacuum bottles, by water displacement, or by aspirating devices and sampling bottles. It would be necessary to analyze samples for sulfides and sulfur dioxide at the source, as analysis of transmitted samples is impossible. A rapid and convenient method for determining hygienically significant concentrations of SO_2 in air is described by Pearce and Schrenk in Bureau of Mines Report of Investigation 4282. The method is not suitable for determining concentrations of less than 2 p.p.m. of SO_2 and is not applicable in atmospheres where SO_2 is present with other reducing or oxidizing gases.

As far as the author knows, no studies have been made to correlate the progress of a mine fire in terms of sulfide or sulfur dioxide; hence, interpretation of the analyses for these gases would be difficult. Utilization of the Ostwald combustion charts and the Pigrais chart is useful in combustion work and may have some application in the determination of SO_2 (7, 19, 24, 25) in some metal-mine-fire atmospheres. It would be interesting for someone to make a study in the field with laboratory methods for sulfides and sulfur dioxide to see if there is any trend after sealing a mine-fire area. Such a problem would be in the nature of research rather than routine analysis.

Pyrite is able to unite with oxygen in the presence of moisture at ordinary atmospheric temperatures. The combination of pyrite with oxygen at atmospheric temperatures to form sulfate not only liberates heat but causes an increase in volume, tending to split rock particles and increase disintegration; this results in increasing the rate of oxidation of the pyrite-bearing rock itself; however, it is observed that enormous piles of concentrates (zinc sulfides or lead sulfides) stand for years without heating. Tailing piles containing all pyrite from mill tailings do not ignite or heat unduly. It is observed that most SO_2 is given off before sintering beds reach a temperature of 1,472° F. (800° C.).

FIRE IN GOLD MINE - MOTHER LODE

A fire was discovered on February 15, 1938, in the underground workings of the Argonaut mine, Jackson, Calif. This fire has been briefly described (1).

The Argonaut mine is one of the deepest and most widely known gold mines in the world. It adjoins the Kennedy mine and is separated from it by a small barrier pillar. By mutual agreement, the two mines are connected by a refuge chamber placed 4,800 feet vertically from the shaft portals. The ore body consists of a quartz vein ranging in width from a few inches to more than 60 feet. The walls are greenstone and slate. These strata are metamorphic rocks and are methane-bearing. Large volumes of methane have been found. An overhead method of stoping is utilized requiring square-set timbers, which are backfilled with waste. The filled stopes and large amount of timber make sealing or flooding necessary to prevent a fire from spreading if it reaches the stope workings.

The Argonaut mine was one of the best-ventilated mines in California. Primary ventilation was achieved by placing an exhaust fan at the portal of the Muldoon shaft. Under natural ventilating conditions the main shaft was upcast, but it was considered practical and necessary to operate it downcast. The adjoining Kennedy mine shaft was both normally and naturally operated as a downcast shaft.

The mine fire occurred on the 4,350-foot level from an unknown cause on February 15; it was sealed on February 26 - 11 days after the fire was discovered. Natural rock temperatures in the lower mine workings are 92° F.

The mine air under seal was sampled systematically at several points. By March 17, 1938, events indicated that a change of pressure at the Muldoon fan was affecting the samples; it was necessary to collect samples of the atmosphere nearer the fire zone and stop probable leaks at the Kennedy 3,300-foot-level cross cut and in the Argonaut shaft above the 1,250-foot fire doors.

A tight door was placed outby the steel door separating the Kennedy 4,800 level from the Argonaut at the refuge chamber, space being allowed between the doors for 10 men wearing 2-hour oxygen breathing apparatus. Rock temperatures and humidity are high at the Kennedy 4,800 level, and the 4,800 drift and crosscut is blind for some distance between the raises connecting the Kennedy 4,800 level and lower levels. Owing to the high temperature (88° at 100-percent humidity), it was an arduous task to travel this distance with or without apparatus, and it developed from experience that it would have been impossible to sample the gases in the Argonaut 5,700 level if provisions had not been made to provide fresh air (in motion) at the air lock. A 6-inch Lamb Air-Foil injector blowing 2,000 cubic feet of air per minute was placed in the last raise connecting the Kennedy 4,800 and 4,950 levels, and metal tubing was extended to a point outby the air lock, which was established as a fresh-air base for a reserve crew of six men wearing 2-hour oxygen breathing apparatus.

On March 29, two crews of six men each were selected from the personnel of the Argonaut and Kennedy mines. Previous tests established that no dangerous concentration of methane was present, and an apparatus crew of six men (under oxygen) entered the air lock, broke the seals to the Argonaut mine, and entered and explored the refuge chamber and the Argonaut section. Humidity readings and samples of the mine air were taken, and the carbon monoxide supersensitive indicator operated for 20 minutes. Temperatures at the fresh-air base were 88° wet bulb and 91° dry bulb; in the Argonaut mine, 92° wet bulb and 92° dry bulb. The pressure on the seal was negative, and a safety lamp placed in the air lock remained lighted. When the first crew returned, the second crew of six men entered the air-lock under oxygen and replaced the mine seals.

The fire zone cooled rapidly during the week of April 1. The pressure at the Kennedy 4,800 seal was observed to be changing from negative to positive for the first time. Black damp extinguished the flame of a safety lamp at the sampling pipe; this indicated that the high-density gases in and above the active fire zone were readjusting themselves, and their density was increasing enough to move them to displace the lighter density gases in the Argonaut mine below the active fire zone. This readjustment of the heavy atmosphere materially changed the pressure from negative to positive on the Kennedy mine seals. This was the first definite indication that the fire was extinguished.

On April 8, as on March 29, crews wearing 2-hour oxygen breathing apparatus entered the Argonaut mine through the Kennedy-4,800, Argonaut-5,700 refuge chamber connection and made tests of the atmosphere.

The pressure on the Kennedy seal now was constantly positive, and the flame of a safety lamp placed in the air lock was extinguished immediately by gases entering through the refuge chamber door, which was slightly ajar to allow passage of the life line. Temperatures at the Kennedy-side fresh-air base were 88° wet bulb and 89° dry bulb and 91° wet bulb and 92° dry bulb in the Argonaut mine. Before the crew completed its tests and returned, the air from the Argonaut flowed through unavoidable leaks and decreased the oxygen content of the mine air at the fresh-air base so much that the flame of a safety lamp was extinguished, and a carbide light failed to burn at a point waist-high, which showed the value of taking fresh air to this point by the Lamb Air-Foil injector and metal tubing. This noxious-air condition disappeared when the seals were closed. The carbon monoxide supersensitive indicator showed no carbon monoxide during the tests. Arrangements were made to reopen the mine on April 15, just 2 months after the fire was discovered.

The importance of deductions from analyses of mine-fire atmospheres and from the pressure exerted by them on seals in a mine-fire area is not always realized. Whether the pressure on a seal is positive or negative depends primarily on the difference between the specific gravities of the atmospheres on opposite sides of the seal. A cooled mine-fire atmosphere sometimes becomes heavy enough to overcome the normal ventilating motive column.

It cannot be expected that the composition of the atmosphere will be uniform throughout a sealed area, and it is important to have several sampling points where accurate samples can be collected (3).

Because of the differences in magnitude of the specific gravity and percentage of the respective simple gases composing a mine-fire atmosphere, the air-free compositions of different portions of an atmosphere confined in a place with which the mine-fire atmosphere is mixing by convection and diffusion differ from each other and from the air-free mine-fire atmosphere. For this reason it is often desirable to know the specific gravity of portions of the sealed atmosphere (3).

A brief discussion of analyses of some samples collected in the sealed fire area in the Argonaut mine will serve as an example of the foregoing subject.

The weight of 1 liter of a given gas at 0° C. and 760 mm. pressure is found by the following formula:

$$\text{Weight of 1 liter of given gas} = \frac{(\text{molecular weight of given gas})\ (1.42904)}{32}.$$

The specific gravity of a given gas, when the specific gravity of air is 1, is found by the following formula:

$$\text{Specific gravity of given gas} = \frac{\text{weight of 1 liter of given gas}}{1.2929}.$$

The arithmetical calculations concerning the specific gravities of the selected samples are not given; however, the specific gravities have been calculated, and the procedure employed to determine them is summarized in the following table, which gives the real values relating to one of the samples:

Composition of mine-fire atmosphere at Argonaut gold mine

		Analyses (percent)									
		As received					Air-free				
Date	Place	CO_2	O_2	CH_4	CO	N_2	CO_2	CH_4	CO	N_2	Remarks
2/23/38	Muldoon fan	2.22	18.54	0.22	0.12	78.90	19.56	1.93	1.05	77.46	Upcast 4,350 ft. Above fire.
3/10/38	do.	11.95	3.90	.25	.07	83.83	14.67	.31	.09	84.93	Do.
3/31/38	do.	11.60	3.60	.05	.02	84.73	14.01	.06	.04	85.89	Pressure positive.
4/8/38	do.	5.70	13.24	.01	.00	81.05	15.51	.03	.00	84.46	Pressure oscillatory.
3/29/38	In refuge chamber	7.43	10.12	.06	.01	82.38	14.47	.12	.02	85.39	Taken by crew under oxygen 1,350 ft. below fire; pressure negative on bulkhead.
4/8/38	do.	12.54	2.95	.10	.00	85.41	14.62	.12	.00	85.26	Same place, but pressure positive on bulkhead. This is a complete reversal of normal ventilating conditions.

Mine unsealed April 15, 1938. Fire out.

Physical qualities of constituents of mine-fire gas, procedure to determine specific gravity of this gas,[1] and specific gravity of one definite sample.

Gas	Formula	Molecular weight (based upon atomic weights as of 1941)	Weight, in grams per liter, at 0° C. and 760 mm.	Specific gravity Air = 1	Composition of mine-fire gas (in percent by volume)	Weight (in grams) of the respective volume of each constituent contained in 1 liter of the mine-fire gas
Carbon monoxide..	CO	28.01	1.2504	0.9671	0.01	0.00013
Methane..........	CH_4	16.04	.7168	.5544	.06	.00043
Hydrogen.........	H_2	2.0162	.08988	.06952	.00	.00000
Ethylene.........	C_2H_4	28.05	1.2604	.9749	.00	.00000
Propylene........	C_3H_6	42.08	1.937	[2]1.498	.00	.00000
Ethane...........	C_2H_6	30.07	1.3566	1.0493	.00	.00000
Carbon dioxide...	CO_2	44.01	1.9769	1.5290	7.43	.14688
Nitrogen.........	N_2	28.02	1.25055	.96724	82.38	1.03020
Oxygen...........	O_2	32.00	1.42904	1.10527	10.12	.14462
Definite sample[3]	Mixture of some above-given gases.		1.32226	1.022	100.00	1.32226

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[1] Handbook of Chemistry and Physics, 28th edition, 1944.

[2] Lange's Handbook of Chemistry, 1946.

[3] Sample collected in refuge chamber on 3/29/38. (See table covering composition of mine-fire atmosphere, and the following table.)

Summary of specific gravities of pertinent samples (as received) of mine-fire atmospheres, Argonaut mine

Date	Place	Analysis, as received, percent					Specific gravity
		CO_2	O_2	CH_4	CO	N_2	
1938	Normal atmospheric air	0.03	20.93	0.00	0.00	79.04	1.000
3/31/38	Muldoon fan, surface	11.60	3.60	.05	.02	84.73	1.037
4/8/38	Muldoon fan, surface	5.70	13.24	.01	.00	81.05	1.017
3/29/38	Refuge chamber, undergr.	7.43	10.12	.06	.01	82.38	1.022
4/8/38	Refuge chamber, undergr.	12.54	2.95	.10	.00	85.41	1.052

From the foregoing data, it is observed, from samples taken at the Muldoon fan (4,350 feet above the active fire) and in the refuge chamber (1,350 feet below the active fire) on March 31 and March 29, respectively, that the mine air at the fan and in the refuge chamber was heavier than normal air at 0° C. and 760 mm. pressure; however, because the air at the fan actually was rarer at existent temperatures because of heated conditions, the pressure on the refuge-chamber bulkhead was negative. By April 8, the area had cooled considerably, and the carbon dioxide was settling to the lowest parts of the mine more rapidly than it was diffusing into the mine air; this is shown by the increased specific gravity of the mine air in the refuge chamber. It was 1.052 (the highest in the mine) and was evidenced by the pressure becoming positive on the refuge-chamber bulkhead. The fact that the air in all parts of the Argonaut mine was heavier than the normal air in the Kennedy mine caused it to flow toward the Kennedy mine and yielded conclusive evidence that the fire was out and that it was safe to unseal the mine. This conclusion was verified when the mine was unsealed on April 15, 1938, and the fire was found to be out.

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